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(54) SILICATE COATED POLYMERIC SHAPED OBJECTS

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APPLICATION FOR LETTERS PATENT

by James L. Hecht and Ralph K. Iler

Silicate Coated Polymeric Shaped Objects

Abstract of the Disclosure

Organic polymeric shaped objects, such as films, coated with lithium silicates having a specific composition ratio, and a process for their preparation using aqueous colloids of the coating material.

Background of the Invention

In the preparation of thermoplastic polymeric films and the like, it is often necessary to modify the permeability or surface characteristics of the finished product to impart characteristics not exhibited by the film itself. Accordingly, many different classes of coating materials have previously been used to modify the characteristics of thermoplastic materials. Of the inorganic materials used for coating, continuous, glassy coatings are known to provide excellent moisture and gas barrier properties. However, such materials are generally difficult to apply to the polymer surface.

Summary of the Invention

The present invention provides coated structures having improved moisture and gas impermeability which are easily and economically prepared.

Specifically, the instant invention provides an organic, polymeric shaped article having a substantially continuous, gas and liquid-impermeable coating on at least one surface thereof, the coating comprising lithium silicate having a mole ratio of SiO_2 to Li_2O of about from 1.6/1 to 4.6/1.

Preferably, coated films of the invention further comprise a heat-sealable polymeric coating applied over the silicate coating.

The coated shaped articles can be prepared by applying to an organic, polymeric shaped article an aqueous dispersion of lithium silicate wherein the mole ratio of SiO_2 to Li_2O is about from 1.6/1 to 4.6/1, and drying the coated film at elevated temperatures to remove excess water.

Brief Description of the Drawing

Figures 1 and 2 are cross sectional illustrations of representative coated films of the instant invention, the layers of the films not being drawn to scale.

Figure 3 is a graphical representation of the effect of the SiO_2/Li_2O mole ratio of the coating composition on gas barrier properties.

Detailed Description of the Invention

Shaped articles which can be used in the instant invention include films, containers, bottles, fibers and the like prepared from polyesters, polyolefins such as polypropylene and polyethylene and copolymers thereof including ionomers, the perfluoro polymer prepared from tetrafluoroethylene and hexafluoropropylene, polyacrylonitrile, polyvinyl chloride, polyvinylidene chloride, polyvinyl fluoride, polystyrene, polyimides, polyamides, cellulose acetate and the like. Of these, polyester films such as oriented heat set polyethylene terephthalate and oriented linear polypropylene films are particularly preferred. The polymer used as a base in the present invention is preferably water-insensitive. That is, that the polymer should not undergo a substantial change in dimension or structural integrity when exposed to the aqueous dispersions that can be used to apply the barrier coatings of the instant invention.

The coatings of the instant invention consist essentially of the lithium silicate. It has been found that these compositions provide excellent gas and moisture barrier properties for thermoplastic films when the mole ratio of SiO_2 and Li_2O is about from 1.6/1 to 4.6/1. In addition, it

has been found that particularly satisfactory barrier properties are obtained with SiO_2/Li_2O mole ratios of about from 3.2/1 to 4.2/1, and such coatings are therefore particularly preferred.

According to the instant invention, the lithium silicate can be applied to the polymeric substrate in the form of an aqueous colloidal dispersion. The dispersion can be prepared from available lithium silicate compositions, such as that commercially available from E. I. du Pont de Nemours and Company as "Lithium Polysilicate 48". This composition is an aqueous solution of SiO_2/Li_2O having a ratio of about 4.8/1 and having about 20% by weight of SiO_2. This composition, after dilution with water to the desired solids content, can be adjusted as to Li_2O/SiO_2 ratio by the addition of lithium hydroxide. After the addition of the required amount of lithium hydroxide, for best barrier properties, the mixture can be heated, for example, to 70°C., and maintained at this temperature for 1/2 hour, and then cooled to room temperature.

The concentration of the dispersion is not critical to the invention and can be adjusted to satisfy the requirements of coating apparatus used and final coating thickness desired. In general, the dispersions have a solids content of less than about 8%, when used with kiss or doctor roll coating techniques.

The colloidal dispersion can also contain additives such as resins that improve the wettability and adhesion of the coatings to the base to which they are applied. Additives which have been found particularly effective in this application include melamine-formaldehyde resins, urea-formaldehyde resins, polyethylenimine, and amino acids such as glycine and

alanine alone or in combination. In general, up to about 50%, by weight of the silicate, of such additives can be used in the coating. The additive is conveniently incorporated into the dispersion after the adjustment to the required mole ratio.

The dispersion can be coated onto one or both sides of the substrate using any conventional coating technique including, for example, kiss coating, doctor rolls, gravure rolls, immersion coating techniques, spraying, and the like, with or without such expedients as Mayer rods or air doctor knives. The dispersion is preferably applied to the polymeric substrate within a week after preparation, since extended aging of the dispersion depreciates its barrier properties. The coating thickness should be such as to give at least 0.02 g./m.^{2} of the lithium silicate on the coated surface, and preferably about from 0.1 to 0.6 g./m.^{2}. The dispersion can be applied, for better adhesion, to a substrate that has been treated to ionize the surface. Treatments which can be used include flame treatment, electrical discharge treatment, as well as caustic or alkaline etching of the substrate surface. In general, pretreatment by conventional flame treatment is preferred. However, when a resin additive is used in the dispersion, the need for ionization of the base surface is frequently eliminated.

After application of the dispersion, the coated substrate is dried at elevated temperatures to remove water from the dispersion. Drying times and temperatures will vary widely, depending, for example, on the composition of the base polymeric article, the concentration of the coating sol, the coating thickness, and the air flow in the drier. Coated films are conveniently dried by passing through a tower with radiant heat and countercurrent air flow.

After completion of the drying of the lithium silicate coating, the coated film can be further treated by priming and applying a sealable topcoat of a polymeric material such as polyethylene, vinylidene chloride polymers and copolymers, and ethylene vinyl acetate. Priming agents that can be used include silanes, polyurethanes, aqueous solutions of melamine formaldehyde resins, and aluminum chlorhydroxide. The top coating can be applied by solvent coating, conventional melt extrusion techniques, hot lamination of a preformed film of the heat sealable polymer, or polymer dispersion. It has been found that the barrier properties of films of the invention are often improved when sealable polymer topcoats are applied, beyond the expected additive effect of the two coatings. In addition, the application of a sealable polymer topcoat results in a marked improvement in the retention of barrier properties of the present coatings after repeated flexing. The application of such topcoats is therefore preferred.

The coated articles of the invention, and particularly films, exhibit remarkably improved moisture and gas impermeability. The present coated films are therefore well suited for packaging applications in which moisture and gas impermeability are desired.

The invention is further illustrated by the following examples.

<u>Examples 1-4</u>

In Examples 1-4, lithium silicate solutions were prepared using "Lithium Polysilicate 48" commercially available from E. I. du Pont de Nemours and Company, containing 20% by weight of SiO_2 and having a SiO_2/Li_2O ratio of about 4.8/1.

The solution was diluted with water to varying extents as indicated in Table I, and the SiO_2/Li_2O ratio was adjusted to varying extents by the addition of lithium hydroxide, also as indicated in Table I. The mixtures were heated to 70°C. for 1/2 hour and then cooled to room temperature. The coatings were applied to oriented heat set polyethylene terephthalate film having a thickness of 1.5 mils. The polyethylene terephthalate films were flame treated prior to coating with oxidizing or reducing flames having a ratio of propane to oxygen of from 0.95 to 1.10. The coating solutions were applied by a doctor roll at varying speeds and thicknesses. The coating thickness in each case was determined by the conventional ash method.

Additional samples of the films were laminated to low density polyethylene films, having a thickness of 2 mils, after treatment to promote adhesion.

The film samples were all dried and tested for oxygen and moisture permeability, and the results indicated in Table I.

The coated film of Example 2 was subjected to 20 flexes in accordance with the Gelbo flex test, and the oxygen permeability after testing is indicated in Table I. In addition, the oxygen permeability of those samples additionally laminated to polyethylene and subjected to 20 flexes in the Gelbo flex test was determined and these results additionally indicated in Table I.

The oxygen permeability of Examples 1-4, together with the permeability of other examples of the invention similarly prepared as well as illustrative control samples, is graphically illustrated in Figure 3.

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TABLE I

Example	% Solids, in Bath	SiO_2/Li_2O Ratio	Coating Speed(fpm)	Coating Thickness % Ash	Oxygen Permeability(1)				Moisture Permeability(2)	
					Coated Film	After Flexing(3)	PE Laminate	PE Laminate After Flexing(3)	Coated Film	PE Laminate
1	6.8	3.2	39	1.31	0.12	--	0.14	0.26	8	12
2	3.4	2.5	25	0.54	0.08	0.24	0.09	0.13	28	14
3	3.4	1.8	39	0.87	0.16	--	0.05	0.07	18	13
4	1.7	2.5	39	0.41	0.17	--	0.05	0.19	35	16

(1) CC./100 in.^{2} - 24 hrs. atm. for oxygen permeability, as measured on an Ox-Tran* 100 oxygen permeability analyzer available from Moxem Controls, Minneapolis, Minnesota.

(2) Grams/100 m.^{2} hr. water vapor permeation, as measured by the method described in U.S. Patent 2,147,180.

(3) Gelbo Flex Test (according to P.A. Gelber et al., "Modern Packaging," January 1952, page 125).

* denotes trademark

Example 5

The general procedure of Examples 1-4 was repeated using a lithium silicate having a SiO_2/Li_2O ratio of 2.5. The film was coated with a normal thickness of vinylidene chloride copolymer and tested. The topcoated film was found to exhibit an oxygen permeability of less than 0.05 cc./100 in.^{2}/24 hrs./atm., and a moisture permeability of 8 grams/100 m.^{2}/hr.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A water insensitive, organic, polymeric shaped article having a substantially continuous, gas and liquid-impermeable coating on at least one surface thereof, the coating comprising lithium silicate having a mole ratio of SiO_2 to Li_2O of about from 1.6/1 to 4.6/1, said coating being at least 0.02 g lithium silicate per square metre of coated surface.

2. An article of Claim 1 wherein the shaped article is a film.

3. An article of Claim 1 wherein at least one surface of the shaped polymeric article is flame treated prior to the application of the silicate coating.

4. An article of Claim 1 wherein the coating further comprises up to about 50%, by weight of the coating, of adhesion promoting additive.

5. An article of Claim 4 wherein the adhesion promoting additive is selected from melamine-formaldehyde resins, urea-formaldehyde resins, polyethyleneimine, glycine and alanine.

6. An article of Claim 2 further comprising a heat-sealable topcoat on at least one surface of the film.

7. An article of Claim 1 wherein the mole ratio of SiO_2 to Li_2O is about from 4.2/1 to 3.2/1.

8. The process for the preparation of coated shaped articles comprising applying to an organic, polymeric, shaped article an aqueous dispersion of lithium silicate, wherein the mole ratio of SiO_2 to Li_2O is about from 1.6/1 to 4.6/1, and drying the coated shaped article at elevated temperatures to remove excess water, the coating being at least 0.02 g lithium silicate per square metre of coated surface.

9. The process of Claim 8 further comprising applying a heat-sealable topcoat to at least one surface of the shaped article.

10. The process of Claim 8 wherein the shaped article is a film.

FIG. 1

FIG. 2

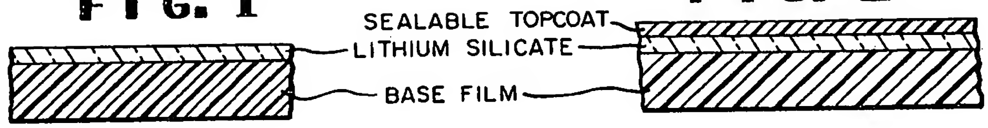
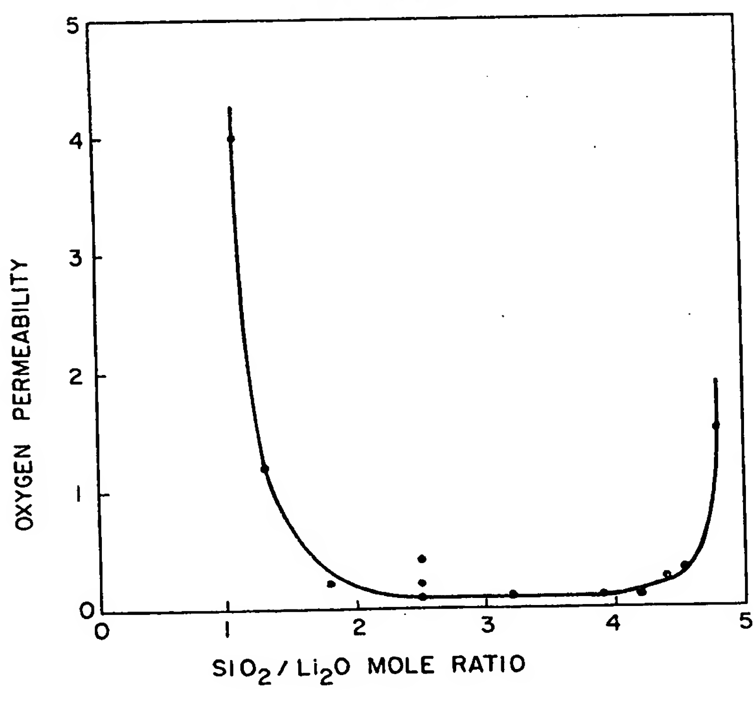


FIG. 3



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